Shining new light on photoresponsive polymers: orthogonal molecular photoswitches for the construction of functional polymeric materials

The eye is a sophisticated organ of the human body, which has inspired scientists throughout history. One of the proteins found in the eye is rhodopsin, which is responsible for vision. The key element of rhodopsin is 11-*cis*-retinal, which undergoes isomerisation to *trans*-retinal when exposed to light. Retinal photoisomerization constitutes an archetype of **molecular photoswitches**, which are molecules capable of reversibly "switching" between two stable states upon exposure to light of an appropriate wavelength. One attractive possibility is the construction of a system that incorporates two switches. A **photo-orthogonal system** can be created using an appropriately selected molecular switches. Photo-orthogonality implies that at least two switches can operate independently from each other and can be isomerized in any order. A material containing the described system can exist in at least four distinct states (Fig. 1). The human eye utilises a similar system containing a series of complex proteins called opsins, which respond to different ranges of electromagnetic radiation and serve as the foundation for colour vision.

One possible approach for creating a synthetic orthogonal system is to incorporate molecular photoswitches into polymeric materials. Polymers are present in almost every aspect of daily life, ranging from the plastic bags used for packaging to advanced materials used in sophisticated electronic devices. **Block copolymers** are a class of polymers comprising at least two units that are arranged in segments. **Amphiphilic** block copolymers consisting of both hydrophilic and hydrophobic blocks can **self-assemble** and undergo spontaneous ordering to form larger structures. New opportunities have emerged for the design of functional materials by incorporating elements within block copolymers that can undergo reversible changes under the influence of light.

The objective of this project is to obtain **photoresponsive thin films and membranes based on an azobenzene and spiropyran photo-orthogonal system incorporated into amphiphilic block copolymers** and to investigate their physicochemical and photochemical properties, as well as their self-assembly into ordered structures. Block copolymers will be synthesised through atom transfer radical polymerisation (ATRP). Thin films and membranes will be fabricated using solvent-assisted directed self-assembly (DSA-SNIPS) methods. The project will employ a range of experimental techniques, including thermal analysis, spectroscopic methods, scattering methods, microscopy, spectrometry, and a combination of these techniques along with simultaneous light irradiation.

As a result, a new concept of the photo-orthogonality of molecular switches in materials based on amphiphilic BCPs will be introduced, expanding our knowledge of their photochemistry and self-assembly. The success of the project can provide new tools for constructing "*smart materials*" which are among the rapidly developing trends in the chemical sciences. These materials include nanoporous membranes that are utilised in gas separation, medicine (controlled drug delivery and dialysis), and water purification.

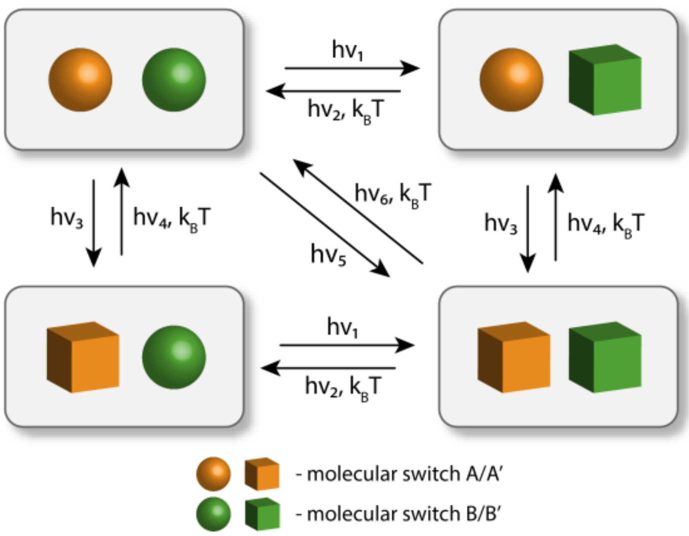

Fig.1: *Schematic representation of photo-orthogonal system.*